UNIVERSITI PUTRA MALAYSIA

KINETICS AND MECHANISM OF CADMIUM, COPPER AND LEAD ION BIOSORPTION USING ASPERGILLUS FLAVUS 44-1 LIVE BIOMASS

KOK KEAN HIN

FSMB 2002 3

KINETICS AND MECHANISM OF CADMIUM, COPPER AND LEAD ION BIOSORPTION USING *ASPERGILLUS FLAVUS* 44-1 LIVE BIOMASS

By

KOK KEAN HIN

Thesis Submitted in Fulfilment of the Requirement for the Degree of Master of Science in the Faculty of Food Science and Biotechnology Universiti Putra Malaysia

June 2002

DEDICATION

Specially dedicated to.

My parents, F.O., Kok and P.H., Yeap

My siblings, S.N., Kok, S.F., Kok and S.Y., Kok

All of my family members

All of my friends

My supervisor, Professor Dr. Mohamed Ismail Abdul Karim

My committee members, Associate Professor Dr. Arbakariya Ariff

Dr. Suraini Abdul Aziz

Thank you for everything.

Abstract of thesis presented to the senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

KINETICS AND MECHANISM OF CADMIUM, COPPER AND LEAD ION BIOSORPTION USING *ASPERGILLUS FLAVUS* 44-1 LIVE BIOMASS

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June 2002

Chairman: Professor Mohamed Ismail Abdul Karim, Ph.D.

Faculty: Food Science and Biotechnology

Study on the feasibility of using live biomass of *Aspergillus flavus* as biosorbent to remove heavy metals, such as cadmium (Cd), copper (Cu) and lead (Pb) from solution was carried out in batch sorption isotherm experiments using 500.0 mL shake flask and 2 L stirred tank reactor. The effect of metal concentration (0 - 480.0 mg/L), biosorbent concentration (0 – 5.0 g/L), pH (pH 1.0 – pH 5.0) and temperature (10.0°C – 60.0°C) were investigated in single (Cd, Cu, Pb) and multimetals (CdCu, CdPb, CuPb, CdCuPb) system. Preliminary study on the biosorption heat of metal ions (Cd^{2+}, Cu^{2+}, Pb^{2+}) on *Aspergillus flavus* was also conducted. Microscopic study using Scanning and Transmission Electron Microscope and X-ray Energy Dispersive analysis were also performed.

Results obtained from single cadmium (Cd), copper (Cu) and lead (Pb) system in the shake flask experiments revealed that biomass of *Aspergillus flavus*

was a potential biosorbent for the removal of Cd, Cu and Pb from solution. Optimum pH for the maximum removal of Cd, Cu and Pb was at pH 2.0, pH 5.0 and pH 4.0, respectively. Optimum temperature for the maximum removal of Cd, Cu and Pb was occurred at 30.0°C, 30.0°C and 40.0°C, respectively. Results from this study also showed that a small amount of *Aspergillus flavus* biosorbent, less than 0.6g, was sufficient to remove a significant large amount of metal ions, almost 23.33 mg/L (Cd^{2+}, Cu^{2+}, Pb^{2+}) from 100.0 mg/L solution.

In the dual (CdCu, CdPb, CuPb) and tri-metals (CdCuPb) system, removal of cadmium (Cd), copper (Cu) and lead (Pb) from solution were interfered by the presence of inhibiting cations. The presence of competing ions have altered the equilibrium state and stability of solution chemistry of the system. The system would shift to another equilibrium in favour of the more influenced ion in the system.

Performance of biosorption in a more controlled surrounding in enclosed contactor, such as stirred tank reactor was preferred by the industry. Maximum lead uptake (59.70 mg/g) by *Aspergillus flavus* in stirred tank reactor could be achieved at pH 5.0, 30.0°C and biosorbent (*Aspergillus flavus*) concentration of 2.0 g/L.

Biosorption data of cadmium (Cd), copper (Cu) and lead (Pb) adsorption in single Cd, Cu and Pb system revealed that the Langmuir, Scatchard and Freundlich models were applicable to the biosorption system. However, the applicability of these adsorption models in the dual(CdCu, CdPb, CuPb) and tri-metals (CdCuPb) system were not encouraging.

Desorption with appropriate eluant (HCl, HNO_3, H_2SO_4) was able to recover the metal ion (Cd^{2+}, Cu^{2+}, Pb^{2+}) from solution and prevent secondary pollution to our environment. The possibility of regenerating the adsorbent (*Aspergillus flavus*) have led to the development of this promising technology.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KINETIK DAN MEKANISMA BIO-PENJERAPAN ION KADMIUM, KUPRUM DAN PLUMBUM DENGAN MENGGUNAKAN BIOJISIM HIDUP *ASPERGILLUS FLAVUS* 44-1

Oleh

KOK KEAN HIN

Jun 2002

Pengerusi: **Profesor Mohamed Ismail Abdul Karim, Ph.D.**

Fakulti: **Sains Makanan dan Bioteknologi**

Kebolehan biojisim hidup *Aspergillus flavus* sebagai biopenjerap dalam pengasingan logam-logam berat seperti kadmium (Cd), kuprum (Cu) dan plumbum (Pb) daripada larutan telah dikaji menggunakan ujikaji penjerapan isoterma tidak selanjar dalam kelalang kon 500.0 mL dan tangki pengaduk 2 liter. Kesan kepekatan logam (0 – 480.0mg/L), kepekatan biopenjerap (0 – 5.0g/L), pH (pH 1.0 – pH 5.0) dan suhu (10.0°C – 60.0° C) telah diselidik dalam ekperimen sistem satu logam (Cd, Cu, Pb) dan sistem pelbagai (CdCu, CdPb, CuPb, CdCuPb) logam. Penyelidikan awal pada haba biopenjerapan oleh ion logam (Cd^{2+}, Cu^{2+}, Pb^{2+}) terhadap *Aspergillus flavus* telah diselidik. Kajian mikroskopik dengan menggunakan mikroskop elektron pengimbas dan penembus serta kajian pengagihan tenaga sinar X telah juga dijalankan. Kajian kinetik dengan penggunaan pelbagai model penjerapan isoterma seperti Langmuir, Scatchard and Freundlich telah dikaji.

Keputusan diperolehi daripada sistem satu logam (Cd, Cu, Pb) dalam eksperimen kelalang kon menunjukkan biojisim *Aspergillus flavus* berpotensi digunakan sebagai biopenjerap dalam pengasingan kadmium (Cd), kuprum (Cu) dan plumbum (Pb) daripada larutan berbanding dengan penjerap yang lain. pH optima dalam pengasingan maksima Cd, Cu dan Pb daripada larutan adalah pada pH 2.0, pH 5.0 dan pH 4.0, manakala suhu optima dalam pengasingan maksima Cd, Cu dan Pb daripada larutan berlaku pada suhu 30.0°C, 30.0°C dan 40.0°C. Kajian juga menunjukkan penggunaan biopenjerap (*Aspergillus flavus*) dalam kuantiti yang rendah, kurang daripada 0.6g, sudah memadai dalam pengasingan maksima logam-logam berat (Cd, Cu, Pb), hampir 23.33mg/L daripada 100.0mg/L larutan dan penambahan biopenjerap (*Aspergillus flavus*) tidak diperlukan.

Bagi pengasingan sistem dua (CdCu, CdPb, CuPb) dan tiga logam (CdCuPb), pengasingan kadmium (Cd), kuprum (Cu) dan plumbum (Pb) daripada larutan telah dipengaruhi oleh kehadiran kation pengganggu. Kehadiran ion penyaing ini telah mengubah keadaan keseimbangan dan kimia larutan sistem tersebut. Sistem tersebut akan berubah ke satu keadaan keseimbangan yang bersesuaian di mana ia lebih berpihak kepada ion penyaing yang lebih berpengaruh.

Keberkesanan proses biopenjerapan di dalam keadaan terkawal, seperti di dalam pengaduk tertutup dan secara amnya merujuk kepada tangki pengaduk, lebih diberi perhatian oleh pihak industri. Maksima penjerapan plumbum (59.70mg/g) oleh *Aspergillus flavus* di dalam tangki pengaduk boleh diperolehi pada pH 5.0, 30.0^{0}C dan pada kepekatan biopenjerap (*Aspergillus flavus*) sebanyak 2.0 g/L.

Data biopenjerapan untuk penjerapan kadmium (Cd), kuprum (Cu) dan plumbum (Pb) di dalam sistem satu logam (Cd, Cu, Pb) menunjukkan model penjerapan isoterma Langmuir, Scatchard dan Freundlich boleh digunakan untuk menjelaskan kinetik proses biopenjerapan ini. Walau bagaimanapun, penggunaan model-model penjerapan isoterma ini dalam sistem dua (CdCu, CdPb, CuPb) dan tiga logam (CdCuPb) tidak bersesuaian.

Proses penyahjerapan dapat dilakukan dengan agen penyahjerap yang sesuai (HCl, HNO_3, H_2SO_4) dan boleh mengelakkan pencemaran sekunder terhadap alam sekeliling serta kitar semula bahan penjerap(*Aspergillus flavus*) dalam proses yang seterusnya. Keupayaan bagi penggunaan semula biopenjerap telah membuka peluang baru dalam perkembangan seterusnya dalam bidang teknologi ini.

ACKNOWLEDGEMENTS

For the hard time that have
been history yesterdays,

…….Daylight I must wait for the sunrise

I must think of a new life

And I mustn't give in

When the dawn comes

Tonight will be a memory too

And a new day will begin……………….T.S. Eliot & Trevor Nunn

First of all, I wish to express my deepest gratitude to my supervisor, Professor Dr. Mohamed Ismail Abdul Karim for his invaluable guidance, constant encouragement and constructive ideas throughout the course of this study. His patience and willingness to look into all of my problems, when I held in the bottlenecks of my study, really assist me lots. I wish to express my thankfulness to Professor Ismail again for his advice and moral support during my days of up and down. I really appreciate it !

My appreciation and gratitude also go to other members of my supervisory committee, Associate Professor Dr. Arbakariya Ariff and Dr. Suraini Abdul Aziz for their guidance and valuable comments during my study. Sincere thanks are also extended to Associate Professor Badlishah Sham Baharin, Dr. Lee Kong Hung, Dr. Foo Hooi Ling, Associate Professor Dr. Mohamed Ali Hassan, Dr. Rosfarizan Mohamed, Associate Professor Dr. Yazid Bin Abdul Manap and Dr. Kamariah Long for their not much, but valuable advice and encouragement.

I also wish to express my appreciation to Encik Rosli Alim, Encik Azman, Puan Aluyah and the staffs in the Fermentation and Bioprocess Engineering laboratory, Enzyme and Bioprocess Engineering laboratory, Waste and Bioprocess Engineering laboratory and Biochemistry laboratory for their support and assistantship throughout my study. My appreciation also extended to Mr. Ooi and Mr. Chan of Food Technology Center, Malaysian Agricultural Research and Development Institute for their guidance to assist me in better understanding of the Flame Atomic Absorption Spectrophotometer. Thanks also extended to Encik Karim of Department of Soil Science, Faculty of Agriculture, Universiti Putra Malaysia for his guidance to enhance my skill in performing the Flame Atomic Absorption Spectrophotometer. My appreciation also extended to Associate Professor Dr. Fauziah Othman and the staffs, especially Mr. Ho, Puan Faridah, Cik Azilah and Puan Siti Selena of Electron Microscopic Unit, Enzyme and Microbial Technology Laboratory, Institute of Bioscience, Universiti Putra Malaysia for their guidance during my practice on the Environmental and Variable Pressure Scanning Electron Microscope, Transmission Electron Microscope and X-ray Energy Dispersive analysis. Not forgetting the other staffs, such as Mr. Ooi, Encik Sobri, Encik Rezal, Encik Bazli and others in Fermentation Technology Unit, Enzyme and Microbial Technology Laboratory, Institute of Bioscience, Universiti Putra Malaysia for their assistantship in carry out the bioreactor system. I would also like to express my gratitude to the Ministry of Science, Technology and Environment, Malaysia for funding this study under the Intensification Research of Priority Area Scheme (RM7) for 1 1/2 years.

Heartfelt appreciation is also due to all of the members of the faculty, staffs, fellow postgraduate and undergraduate students of the Department of Biotechnology, Faculty of Food Science and Biotechnology and Institute of Bioscience for their co-operation and assistance during my study.

Finally, I owe my family a debt of gratitude for what's they have sacrifice for me. Thanks for their understanding, care and invaluable support. Not forgetting my friends and colleagues who are always be helpful and blessed me with solutions during our communication.

I certify that an Examination Committee met on 14^{th} June 2002 to conduct the final examination of Kok Kean Hin on his Master of Science thesis entitled "Kinetics and Mechanism of Cadmium, Copper and Lead ion Biosorption using *Aspergillus flavus* 44-1 Live Biomass" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. The members of the Examination Committee for the candidate are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Thesis Supervisory Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

KOK KEAN HIN

Date: 16 AUG 2002

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